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Appendix to Interim Report 1

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## TUNNEL CATHODES FOR MICROWAVE TUBES

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## TUNNEL CATHODES FOR MICROWAVE TUBES

### I INTRODUCTION

As a result of a number of requests for amplification of statements contained in Interim Report 1, this appendix has been prepared.

The Technical Discussion section is divided into several parts, each of which deals with the details of a specific portion of the work.

## II TECHNICAL DISCUSSION

### A. THEORY OF HOT CARRIERS IN SOLIDS

A discussion of a calculation by John J. Quinn of the mean free path of hot electrons in metals was given in Interim Report 1. This dielectric constant calculation by Quinn serves as a convenient starting point for other calculations. It would, of course, be impractical to make an exact analysis of the electron attenuation problem, so a study of the approximations involved is essential. For example, the Quinn analysis is valid only in high density region  $r_s \ll 1$ . The most straightforward way to examine the approximations is to examine Quinn's work directly; this is being done.

It would also be very useful to look at this attenuation question in another way; the imaginary part of the energy from the dielectric constant approach of Quinn arises from real processes, such as the "four electron" process shown in Fig. 1, as opposed to virtual processes.

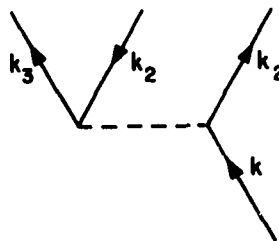


Fig. 1

#### FOUR-ELECTRON PROCESS

The rate at which this four-electron process proceeds can be calculated in a simple way, using the standard time-dependent transition probability method. If the Coulomb interaction were used for the process shown in Fig. 1, the transition probability result would surely give a larger relaxation frequency than Quinn's dielectric constant method, since the

dielectric constant takes into account electron-electron screening. However, if a screened Coulomb interaction--such as the Bohm-Pines screened Coulomb potential--were used, the transition probability method and dielectric constant method should agree more closely. A study of the approximations made in these two methods would give useful insight into the approximations involved in calculating the relaxation frequency; this study is presently under way.

The transition probability method of calculation can be extended in a simple way to include cases other than that of a metal. For example, the problem of calculating the hot electron (or hot hole) mean free path in insulators or semiconductors can be treated in the same manner as in the case of a metal by using a transition probability method. The cases of insulators and semiconductors are extremely interesting, since devices involving electron attenuation in metals often also involve electron attenuation in insulators or semiconductors. The transition probability method of calculating the relaxation frequency of an electron in a semiconductor or insulator will be undertaken in the near future. The expected results of this calculation are as follows: At zero temperature, an electron near the bottom of the conduction band will not be attenuated due to electron-electron interactions. This is because it is impossible to conserve energy and momentum in an electron-electron process in which the original electron is near the bottom of the conduction band. For example, not even energy can be conserved unless the energy of the electron is above the bottom of the conduction band by an amount greater than the gap energy  $E_{\text{gap}}$ ; this is illustrated in Fig. 2, where it is seen that the minimum transfer of energy from the electron having wave vector  $k_1$  originally in the valence band to the electron  $k_3$  in the conduction band is equal to  $E_{\text{gap}}$ . Thus the original hot electron  $k$  must have an energy greater than  $E_{\text{cond}} + E_{\text{gap}}$  in order that it can lose the same amount of energy  $E_{\text{gap}}$ . The fact that momentum also must be conserved requires an even higher energy than  $E_{\text{gap}}$ . When the energy of the original hot electron becomes much greater than  $E_{\text{gap}}$ , the relaxation frequency results for the insulator or semiconductor should go over into the results of the metal.



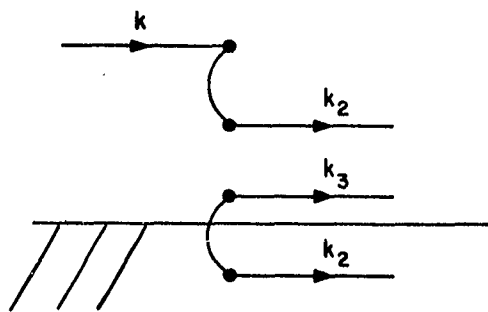


Fig. 2

### SCATTERING PROCESS, ILLUSTRATING ENERGY CONSERVATION

For an electron having a wave vector  $k$  very close to the Fermi level  $k_f$ , the effect of the temperature broadening of the Fermi surface must be considered; in Quinn's analysis, the Fermi surface was assumed to be perfectly sharp, in other words, all states having  $k < k_f$  are full, and all states having  $k > k_f$  are empty. The results of this is that an electron having  $k = k_f$  will have a non-zero relaxation frequency. Very roughly, we expect that the effect of the temperature spread in occupation numbers will be to replace the factor  $(E - E_F / E_F)^2$  by a factor  $(k_{BT} / E_F)^2$ , where  $k_B$  is the Boltzmann constant. The factor  $(k_{BT} / E_F)^2$  arises from the probability that the states  $k_2$  and  $k_3$  are unoccupied. Thus, the temperature effect will be important only for electrons very near the Fermi level. In other words, this temperature effect will be important when the energy of the electron relative to the Fermi surface is of the order of the sample temperature. Since the sample temperature is normally a small fraction of an electron volt, this spread in the Fermi distribution will be negligible in almost all cases.

In addition to the program outlined above, other methods of many-body calculations are presently under study; some of these may be applied to the electron attenuation problem in the future.

## B. EXPERIMENTAL DETAILS ON Nb-Nb<sub>2</sub>O<sub>5</sub>-Hg SYSTEMS

The initial V-I tests on niobium oxide were made using small mercury balls (in the range of 0.5 to 2 mm diameter), dispensed by means of a hypodermic needle. This technique provided a rapid means of determining the range of current densities produced by different formation voltages. The mercury appeared to wet the oxide well, especially around the edges, thus making intimate contact with the oxide (as would an evaporated film of some other metal). However, the mercury apparently did not cause any changes in the oxide itself. The mercury could be completely removed by means of adhesive tape, with no visible effect apparent on the oxide.

The goal was to determine the thickness of niobium oxide that would produce a current density on the order of 1 to 10 amperes/cm<sup>2</sup> at a voltage on the order of 5 to 10 volts. The initial forming voltage used was 10 volts, which produced a current density on the order of 100 amperes/cm<sup>2</sup> at about 3 volts. The forming voltage was then increased to 15 volts. This increased the voltage for 100 amperes/cm<sup>2</sup> to about 4 volts. The forming voltage was then increased to 20, then 25, and finally 30 volts. For each increase in formation voltage, the current density decreased at any given bias voltage. However, instabilities began to set in at 30 volts or higher formation voltage. The current density at 25 volts forming voltage was about 20 amperes/cm<sup>2</sup> at 4 volts bias. This was a somewhat higher current density than desired, but evidently optimum for this structure because of the instabilities noted at higher formation voltages.

At the higher bias voltages and current densities, a gradual discoloration of the niobium oxide was noted. A drift in the I-V characteristics was also observed at the higher current densities, which correlated well with self-heating effects. This gradual drift invariably led to a destructive breakdown of the oxide, leading to a short.

### C. DETAILS OF BARRIER CONSTRUCTION

The following equations are used in constructing the barrier from the experimental I-V data:

$$\phi_m = kT \ln \left[ \frac{120.4 T^2}{J} \left( 1 - e^{-\frac{qV}{kT}} \right) \right] \quad (1)$$

$$q \frac{x_m}{S} = - \frac{d\phi_m}{dV} \quad (2)$$

$$\phi = \phi_m + qV \frac{x_m}{S} \quad (3)$$

where  $\phi$  is the barrier height at any value of  $x$ ,  $\phi_m$  is the maximum barrier height at any given applied voltage  $V$ ,  $T$  is absolute temperature,  $J$  is current density,  $k$  is Boltzmann's constant,  $q$  is electronic charge,  $S$  is barrier thickness,  $x$  is distance through film measured from one of the metal-insulator interfaces, and  $x_m$  is the value of  $x$  at which  $\phi_m$  occurs.

For room temperature and  $\phi$  in electron volts, the above equations can be written

$$\phi_m = 0.025 \ln \left[ \frac{1.013 \times 10^7}{J} \left( 1 - e^{-40V} \right) \right] \quad (4)$$

$$\frac{x_m}{S} = - \frac{d\phi_m}{dV} \quad (5)$$

$$\phi = \phi_m + V \frac{x_m}{S} \quad (6)$$

The procedure used is as follows:

- (a) Measure current vs. voltage at room temperature
- (b) Convert current to current density
- (c) Calculate  $\phi_m$  from Eq. (4) and plot  $\phi_m$  vs.  $V$
- (d) Graphically determine  $d\phi_m/dV$  by measuring the slope of the  $\phi_m$  vs.  $V$  curve at various points
- (e) Calculate  $x_m/S$ , using Eq. (5)
- (f) Calculate  $\phi$  from Eq. (6), using the values of  $\phi_m$  from step (c) and the values of  $x_m/S$  from step (e)
- (g) Plot  $\phi$  vs.  $x_m/S$  (or simply  $x/S$ ). This is the barrier.

This procedure is applicable to insulating films that are too thick for tunneling but too thin for the current to be space-charge-limited. In other words, the method works when the current is a thermionic emission current limited by barrier height.

An article describing the above technique has been submitted for publication to the Journal of Applied Physics.

#### D. ELECTRON AFFINITY CALCULATIONS

The barrier between a metal and an insulator is equal to the work function of the metal minus the electron affinity of the insulator. The electron affinity of an insulator (or semiconductor) is defined as the energy required to raise an electron from the bottom of the conduction band to the vacuum energy level.

The work function of niobium is 3.99 volts and that of mercury 4.52 volts. Therefore, neglecting image forces and doping of the insulator, the barrier for the system Nb-Nb<sub>2</sub>O<sub>5</sub>-Hg should be trapezoidal with the barrier on the mercury side higher than the barrier on the niobium side by the contact potential difference between the two metals, or 0.53 volts. A straight line can be drawn on Fig. 2 of Interim Report 1, intersecting

the left ordinate at 0.55 volts and the right ordinate at  $0.55 + 0.53 = 1.08$  volts. Figure 2 of Interim Report 1 should have been marked to indicate that the left ordinate (at  $x/S = 0$ ) represents the interface between the oxide and the niobium, and the right ordinate (at  $x/S = 1$ ) represents the interface between the oxide and the mercury. The departure of the barrier from this idealized trapezoidal barrier is caused by image forces near  $x/S = 1$  and by a combination of image forces and excess niobium in the oxide near  $x/S = 0$ .

The electron affinity of niobium oxide can thus be computed to be 4.52 (the work function of Hg) minus 1.08 (the barrier height at the Hg interface), or 3.44 volts.

#### E. EDGE EFFECTS

A question has been raised concerning the effect of an increased electric field around the periphery of a metal-insulator-metal sandwich upon the current-voltage characteristic of the sandwich. The question is pertinent because the current flowing through the insulating film generally increases rapidly with applied voltage. Thus, even though the area where the field is higher than normal may be small, the contribution to the current from this area could be significant.

A careful study of the problem shows that the effect is very dependent upon the details of the geometry of the sandwich and the mechanism of current flow through the device. For hard insulators, it is safe to assume that unless an avalanche breakdown occurs, the current is carried predominantly by electrons in the conduction band of the insulator. These electrons are excess carriers injected from the negative electrode through (tunneling) or over (thermionic emission) the barrier. In either case, the current depends only on the field at the negative electrode. (For example, this is the reason why a vacuum diode with a sharp probe for one electrode and a large piece of metal for the other electrode is a rectifier.) Figure 3 shows a typical geometry for an anodized metal with an evaporated counterelectrode. When the counterelectrode is positive, the field at the negative

electrode is lower than normal around the periphery. Thus the current contribution from the area around the edges would be very small. When the counterelectrode is negative, however, the increased field at the edges could cause a significant contribution to the total current.

In the case of Fig. 2 of Interim Report 1, the barrier shape from  $x/s = 0$  to about  $x/s = 0.95$  depends on the current-voltage data taken with the counterelectrode metal positive. Thus, there is no "edge effect"

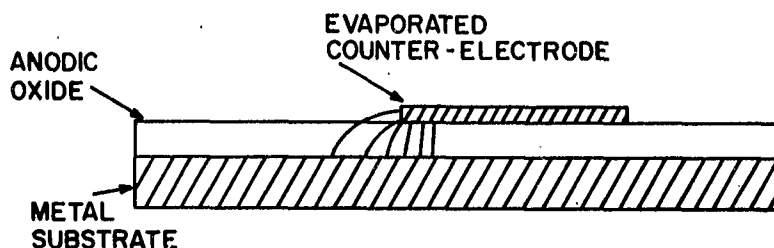


Fig. 3

#### TYPICAL GEOMETRY FOR ANODIZED METAL WITH EVAPORATED ELECTRODE

in this region. The barrier shape from about  $x/s = 0.95$  to  $x/s = 1.0$  depends on the current-voltage data taken with the counterelectrode metal negative, so there could be an "edge effect" in this region. However, this polarity is not of interest for tunnel cathodes, (unless an avalanche condition exists in the film).

#### F. TEMPERATURE CONSIDERATIONS

Current flow through thin insulator films is a very complex subject. For exceedingly thin films, such as 40 Angstrom units or less, tunneling can occur from metal-to-metal at low bias voltages. This current is relatively insensitive to temperature changes, unless the barrier itself changes with temperature, and one can safely assume that metal-insulator-metal barriers are not insensitive to temperature changes. At higher bias voltages, tunneling can occur from the cathode metal into the

conduction band of the insulator; here, another temperature variation can become important, namely the occupation of the traps in the insulator. This factor can be of considerable importance in somewhat thicker insulator films, say greater than 100 Angstrom units, because the tunneling current can become space-charge-limited. This subject is considered in detail in an article "Space-Charge-Limited Tunnel Emission into an Insulating Film," by D. V. Geppert, which appeared in the October 1962 issue of the Journal of Applied Physics.

For insulator films in the range from forty to several hundred or even several thousand Angstrom units, thermionic emission over the barrier can occur (and predominate over tunneling, except at refrigerated temperatures). For the thicker films and for low barriers, this current can become space-charge limited, as discussed extensively in the literature. For a situation where the traps can be completely filled, this space-charge-limited current is relatively insensitive to temperature changes.

For the thicker films, impact ionization at higher applied voltages can cause an avalanche breakdown, leading to generation of hot carriers (both electrons and holes) in the insulating film.

In comparing tunnel emission with thermionic emission with regard to temperature sensitivity, all of the factors mentioned above must be considered. The following table summarizes, on a qualitative basis, the relative temperature sensitivity of several possible cases. In all cases, the barrier is assumed to remain constant with temperature. Any variations in the barrier with temperature are in addition to the fundamental changes inherent in the structures considered.

Changes in the barrier shape with temperature would affect all cases except Case (5).

Case (5), under trap-filled conditions, is a good candidate for the thin-film cathode because the insulating film can be made relatively thick and because the current is insensitive to temperature changes, even if the barrier changes with temperature. The low barrier required

for this case may necessitate avalanche breakdown conditions in order to generate sufficiently hot electrons for vacuum emission.

Case	Type of Emission	Temperature Sensitivity
(1)	Tunneling from metal-to-metal at low voltages	Relatively insensitive
(2)	Tunneling into the conduction band of the insulator, not space-charge-limited	Relatively insensitive
(3)	Space-charge-limited tunnel emission into the conduction band of the insulator	For traps unfilled, very temperature-sensitive. For traps filled, relatively insensitive.
(4)	Thermionic emission, not space-charge-limited	Very temperature-sensitive
(5)	Thermionic emission, space-charge-limited (relatively low barrier)	For traps unfilled, very temperature-sensitive. For traps filled, relatively insensitive.

The tests on the niobium oxide structures indicated that such structures are an example of Case (4). The studies on the cadmium sulfide structure are inconclusive as yet, but the evidence strongly points to an avalanche breakdown at the higher bias voltages. The unknown factor as yet in this case is the role of space charge.

#### G. BARRIER CHANGES WITH TEMPERATURE

There are good theoretical reasons to believe that the shape of metal-insulator-metal potential barriers change with temperature. At the present time, however, there is insufficient experimental data to attempt to correlate theory and practice. Some data along these lines are being procured on this program, and some insight into this problem may be gained when further data are gathered and analyzed.



#### H. GENERATION OF HOT ELECTRONS WITHOUT TUNNELING

The barrier construction shown in Fig. 2 of Interim Report 1 can be used to compute the tunneling contribution to the total current flow through the niobium oxide film. For example, at 2.5 volts bias, the barrier to tunneling can be constructed by subtracting 2.5 volts from the barrier at  $x/S = 0.8$ , 1.5 volts at  $x/s = 0.6$ , etc. on down to  $x/S = 0$ . When this is done, the resulting barrier to tunneling can be well approximated by a triangular barrier having a height of 0.43 volts and an equivalent electric field of  $2.12 \times 10^5$  volts/cm. Using the Fowler-Nordheim equation (applicable to this case of tunneling into the conduction band), the tunnel contribution can be calculated to be only  $4.75 \times 10^{-35}$  amperes-cm<sup>-2</sup>. This is down by a factor of over  $2 \times 10^{35}$  from the observed current density. Therefore, the tunnel contribution is completely negligible.

Hot electrons are generated in the counterelectrode metal when electrons are accelerated through the insulating film into the metal.

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